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SEPARATION OF MENTHOL FROM PEPPERMINT OIL BY FRACTIONAL DISTILLATION

by

HSON MOU CHANG

A Thesis Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
MASTER OF SCIENCE

Major Subject: Chemical Engineering

Signatures have been redacted for privacy

Iowa State College
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I. SUMMARY

The traditional method of production of menthol is to crystallize it from peppermint oil at a temperature of 0 to -10°C. but about 50% of menthol is retained in the oil. The yield is low and only peppermint oils of high menthol content may be used as raw materials.

In spite of the small boiling point difference between menthol and menthone, these two compounds have been separated from peppermint oil by fractionation in an efficient laboratory-scale column under a pressure of 21 mm. Hg. Two methods of obtaining menthol have been studied.

A. Menthone and other low boiling fractions in peppermint oil were first distilled off and menthol in the residue was crystallized out from an ethyl alcohol solution.

B. Menthol was fractionally distilled over and 78% of menthol in the oil was recovered in the pure state.

The products by both methods met the melting point specification of U. S. Pharmacopoeia. The second method is simpler and may expect to give a higher yield of menthol than the first method. A new process of producing menthol from peppermint oil by fractional distillation seems to have great promise.

II. INTRODUCTION

A. Occurrence of Peppermint Oil

There are two general types of peppermint produced from the fresh flowering tips of mentha piperita, mainly in the United States and Europe, and mentha arvensis, mainly in China and Japan. Peppermint oil is a very important essential oil produced on a commercial scale by steam distillation of the peppermint plant. The yield of oil from mentha piperita is usually about 0.5%, based on the weight of dried plant, and the yield of oil from mentha arvensis may be as high as 2% depending on the climatic conditions, soil, and fertilizer (30).

The American and European peppermint oils are generally used as flavoring agents for confectionery and medicinally as a carminative. The Chinese and Japanese oils, due to their high menthol content, are used as the main source of menthol and the so-called dementholized oil may be used as a substitute for the American peppermint oil. Menthol is used extensively in compounding various medicinal preparations; it is often prescribed in fevers, headaches, coughs, colds, nervous disorders of children, snake and insect bites, and diseases of the nose and throat. It is also used in confectioneries, in toilet articles, and even in cigarettes.

Before 1935 Japan was almost the exclusive supplier of menthol and peppermint oil to the world market and the

production for the years 1921 to 1929 is shown in Table I (16).

TABLE I

Production of Japanese Peppermint, 1921 - 1929

(unit 100 pounds)

Year	Peppermint Oil	Natural Menthol	Dementholized Peppermint Oil
1921	604	272	301
1922	556	249	279
1923	583	263	291
1924	1,004	452	501
1925	1,988	787	873
1926	1,467	660	733
1927	1,411	635	705
1928	1,267	571	633
1929	1,507	679	753

After the outbreak of World War II, the export of Japanese peppermint was completely stopped and China and Brazil became the main suppliers of the world. The Pacific northwest is rapidly becoming one of the principal peppermint oil producing areas in the United States, and recently a research project has been set up in the Washington State College, Pullman, to improve the yield and quality of peppermint oil (9). Due to the low menthol content of American oil coupled with its high price as a flavoring agent at present, it has not been used

to produce menthol. The present world production of natural menthol is estimated at about one million pounds annually.

Synthetic menthol has appeared on the American market but is considered to be unsuitable as a substitute for the natural product for medicinal purposes since the natural product is laevo active while the synthetic is a mixture of d- and l- menthol. The current price for synthetic menthol is $6.00 to $6.40 per pound and for U. S. P. natural product is $9.05 to $9.25 per pound (21).

B. Properties and Constituents of Peppermint Oil

The composition of peppermint oil is extremely complicated. Twenty-two compounds have been identified in American oil (12); the chief constituents are arranged in the order of increasing boiling point as follows:

TABLE II

Melting Points and Boiling Points of the Chief Constituents of Peppermint Oil (19)

Compounds	Chemical Formula	M. P., °C.	B. P., °C.
Iso-valeric aldehyde	C_4H_9CHO	-51	92.5
Acetic acid	CH_3COOH	16.7	118.1
Acetaldehyde	CH_3CHO	-73	139.6
α -Pinene	$C_{10}H_{16}$	-50	156.2
α -Phellandrene	$C_{10}H_{16}$	--	175
Iso-valeric acid	C_4H_9COOH	-37.6	176
Cineol	$C_{10}H_{18}O$	- 1	176.4
Limonene	$C_{10}H_{16}$	-96.9	177.7
l -Menthone	$C_{10}H_{18}O$	- 6.6	209
l -Menthol	$C_{10}H_{19}OH$	43	216
Pulegone	$C_{10}H_{16}O$	--	224
Menthyl acetate	$C_{10}H_{19}C_2H_3O$	--	227

Of these compounds, menthol, menthone, and menthyl esters are the most important constituents in the peppermint oil. The percentages of these constituents and the physical constants of oils from various origins vary widely; they are presented in Table III:

TABLE III

Physical Constants (22) and Compositions (23) of Peppermint Oils from Various Sources

	American Oil	English Oil	Japanese Oil	Chinese Oil (10)
Density (25°C.)	.909 - .920	.901- .912	.895- .902	.890- .905
Optical Rotation (25°C. 100mm)	-23 to -33	-21 to -33	-29 to -42	-29 to -42
Refractive Index (n_D^{20})	1.460-1.471	1.460-1.463	1.460-1.463	1.460-1.465
Solubility (Oil;70% alc.)	1 : 2.5-5	1 : 2-3.5	1 : 2-3	1 : 2-3
% Menthol	47 - 62	42 - 64	60 - 85	60 - 80
% Menthone	17 - 31	29 - 42	15 - 22	12 - 25
% Menthyl esters	4.5 - 11	2.3 -6.2	3 - 6	2 - 6

From these data it is evident that the oil produced in China and Japan has a much higher content of menthol. The menthyl esters and other constituents are relatively low in all of the oils and the chief problem in producing menthol from peppermint oil is the separation of menthol and menthone.

C. Traditional Method of Producing Menthol

The present method of production of menthol in China, Japan, and Brazil is to crystallize the menthol out of pepper-

mint oil at a temperature of 0 to -10°C. Since menthol is very soluble in menthone and other constituents in peppermint oil even at low temperatures, a large portion of menthol is retained in the oil. This so-called dementholized oil contains about 50% menthol and is sold at a price about one-fourth of that of menthol crystals. The yield of menthol by this method drops very rapidly for a small decrease of the menthol content of the original oil. This situation is illustrated in the following examples.

(Basis - 100 pounds of peppermint oil):

1. If the original oil contains 80 pounds menthol and 20 pounds non-menthol constituents, there will be 20 pounds menthol left in the dementholized oil. The yield will be 60 pounds menthol per 100 pounds peppermint oil, or 75% of the menthol is extracted.

2. If the original oil contains only 60 pounds menthol and 40 pounds non-menthol constituents, 40 pounds menthol will be left in the dementholized oil. Only 33⅓ of menthol can be removed.

It is evident that only peppermint oil of very high menthol content may be used for the production of menthol by this method. Since the menthol content of the oil is affected quite seriously by the climatic conditions and varies from year to year, the production of menthol will be greatly decreased if the quality of the crop is not up to normal. Moreover, the menthol content in American and European peppermint oils is

usually below 50% and therefore cannot be used as raw materials for the production of menthol by mere crystallization.

D. Purpose of Study

The purpose of the present investigation is to find a method to separate menthol from peppermint oil beyond the solubility limit so that a much higher yield of menthol may be obtained and peppermint oils of low menthol content of American and European origins may also be used as raw materials for the production of menthol.

The dementholized oil contains about 50% menthol while the price of the former is only 25% of the latter. It seems that a complete separation of menthol from the oil should be profitable even if the residue oil is not utilized and entirely wasted. As menthol is a very expensive chemical, the extra income derived from an increase in yield will allow a reasonable increase in the processing cost.

In the present investigation, separation of menthol from peppermint oil by fractional distillation was studied in a laboratory column. This method was chosen from a number of possible way of solving the problem, because no expensive chemicals are needed and because a separation by physical means is in general more economical than by chemical reactions.

III. REVIEW OF LITERATURE

A. Physical Constants of Menthol and Menthone

Since the key problem in this study is the separation of menthol from menthone, the physical constants of these two compounds were first examined.

Table IV

Physical Constants of Menthol and Menthone (27)(30)

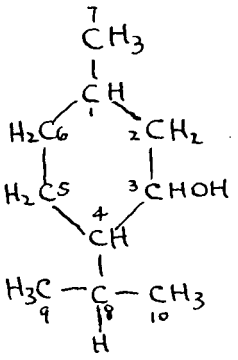
	l-Menthol	l-Menthone
Density (30°C.)	0.8911	0.8946
Melting point	43°C.	- 6.6°C.
Boiling point	216°C.	209°C.
Refractive Index	1.4461 (n_D^{60})	1.4504 (n_D^{20})
Specific Rotation (c = 20, in alcohol)	- 50°	- 28°
Solubility at 20°C.		
1. In water	0.42 g/l	0.69 g/l
2. In ethyl alcohol	Very soluble	∞
3. In ether, CS_2, C_6H_6	Very soluble	∞

The densities and refractive indexes of menthol and menthone are too close together to be employed as accurate criteria in determination of these two compounds. The specific rotations of commercial products vary over quite wide range and are greatly affected by the other constituents present in the oil. Therefore, a satisfactory method of determining menthol and menthone in peppermint oil by physical properties has not been found so far.

B. Chemical Properties of Menthol and Menthone

1. Menthol

Menthol is a secondary alcohol containing a six-membered cyclohexane ring and two substituent groups, methyl and isopropyl.



The carbon atoms are usually designated according to the numbering system indicated by the formula above. The three asymmetric carbon atoms in menthol allow the existence of 8 stereoisomeric menthols, of which five (d and l-menthol, M.P. 43°C., d and

and l-neomenthol, M.P. -22°C., and d-neoisomenthol, M.P. -8°C.) are known. The synthetic menthol from thymol is a mixture of d- and l-menthol and is optically inactive. This racemic mixture has a congealing point at 27-28°C.; after stirring for several minutes, the temperature rises sharply to 31°C.

As an alcohol, the most important reactions of menthol are those of ester formation, oxidation, and reduction.

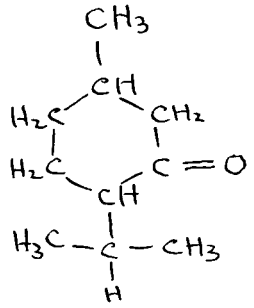
a. Ester formation. Menthol reacts with acetic anhydride or acetic chloride to form menthyl acetate. This reaction is accelerated by the presence of catalysts or by boiling under reflux and is utilized as the basis of analyzing menthol.

b. Oxidation. Menthol may be oxidized to menthone by leading a mixture of menthol vapor and steam over a catalyst at 185°C. to give 96% yield of menthone (17). Another method is to oxidize menthol by chromic-sulfuric acid mixture. The yield was reported to be almost quantitative (31).

c. Reduction. Menthol may be reduced to menthane by first converting it to the iodide and reducing the latter by the usual methods.

2. Menthone

Menthone is the ketone from menthol.



It occurs in the d-form in oil of pennyroyal and in the l-form in peppermint oil.

a. Reduction. Menthone may be reduced to menthol either by hydrogenation in the presence of an active metal catalyst or by using reducing agent such as sodium alcoholate or aluminum isopropylate.

b. Addition. Unlike most other ketones, menthone does not add sodium bisulfite. Thus it is not possible to isolate menthone from the peppermint oil by this reaction.

c. Reaction with hydroxylamine, hydrazine and substituted hydrazines. Menthone reacts readily with these reagents to form the corresponding oxime and hydrazones. These reactions may be employed in the analysis of menthone.

C. Possible Methods of Attacking the Problem

1. Separation of menthone from the oil by chemical means

Menthone reacts with the hydrochlorides of phenyl hydrazine, hydroxylamine, and semicarbazide to form phenylhydrazone, oxime, and semicarbazone respectively. The menthyl phenyl-

hydrazone is partially soluble in the oil while the oxime and semicarbazone are insoluble. The last two derivatives may be separated from the oil readily, but these reagents are too expensive for industrial application. The current price of hydroxylamine hydrochloride is about $5.00 per pound and that of semicarbazide hydrochloride is $12.00 per pound. However, since it requires only about ½ pound of hydroxylamine hydrochloride for each pound of menthone in the oil, the use of this reagent may be feasible if the menthol content in the oil is high compared with the menthone. For example, if the menthone content in the oil is 20% and 60% of menthol is obtainable, the cost of hydroxylamine hydrochloride will be about $0.50 for each pound of oil producing 0.6 pound of menthol, which is worth about $5.70.

2. Conversion of menthone to menthol by reduction

a. Electrolytic reduction. When menthone was reduced electrolytically using alcoholic sulfuric or hydrochloric acid as the electrolyte, menthol, menthane, and α-menthopinacol were formed with the yield of menthol not more than 25% (7). The reduction was found to take place best at cathodes of lead or tin amalgam. Pure mercury was the best cathode, but then the amount of menthane formed was very large. Since the yield of menthol by reduction of pure menthone was not satisfactory, the reduction of peppermint oil by electrolytic method has not been attempted.

b. Reduction using reducing agents. Buhrer (8) reported that the menthone in the peppermint oil might be determined by converting it into menthol using metallic sodium in alcoholic solution as reducing agent and then the total menthol determined as acetate. Lund (20) reduced menthone to menthol using aluminum isopropylate and the yield was 90%. But the presence of other constituents in the peppermint oil introduces many side reactions and the reduction is not so simple as the reduction of pure menthone.

c. Catalytic hydrogenation. The menthone in peppermint oil can be catalytically hydrogenated to menthol, thereby enriching the oil. Various nickel catalysts have been tried (28) but the yield was low. The constituents other than menthol and menthone present in the oil made the reactions very complex and rendered the hydrogenation difficult to be controlled and the results depended on the composition of oil. Although the cost of catalytic hydrogenation is lower than that of using reducing agents, it is necessary to find the optimum conditions and very efficient catalyst to give a selective hydrogenation of menthone without deleterious effect on the menthol.

In general, the reduction of peppermint oil is accompanied by various undesirable reactions which completely change the chemical composition and the valuable properties of the oil. If menthone can be separated out first and then hydrogenated, a good yield of menthol may be obtained.

3. Solvent extraction

Both menthol and menthone were found very soluble in ethyl alcohol, ether, carbon disulfide, glacial acetic acid, chloroform, and carbon tetrachloride. Huntress (15) reported that menthol was very soluble in concentrated HCl but experimental work by the present writer showed that menthol was only very slightly soluble in concentrated HCl even under boiling. Since menthol and menthone are very similar chemically, it does not seem feasible to separate one from the other by the use of organic solvents.

4. Fractional distillation

A number of handbooks report that the boiling point of menthol is 212°C. and that of menthone 209°C. at 760 mm. pressure. With only 3 degrees difference in boiling point, it seems very difficult to separate the two components by fractional distillation at first glance. However, other sources state that the boiling point of menthol at 760 mm. is 216°C., which was verified by the present writer. The boiling point difference becomes even greater at reduced pressures, thus the difference is 15 degrees at 20 mm. and 18 degrees at 5 mm. absolute pressure. By the use of an efficient laboratory scale fractionating column at reduced pressure, it was proved that these two components can be separated satisfactorily from peppermint oil.

In addition, most constituents other than menthol and menthone in peppermint oil have boiling points below 180°C. under atmospheric presure and they can be separated easily from the oil by fractional distillation. These constituents amount to 10-20% of the oil and will retain a large portion of menthol in the oil if they are not separated out before the crystallization. Most experimental work of this research has been performed in this direction and will be discussed later.

IV. METHODS OF ANALYSIS

A. Analysis of Menthol

1. U. S. P. method

The method described in the United States Pharmacopoeia (2) is regarded as the official method of analysis in the trade. The procedure is essentially as follows:

a. Determination of menthyl esters. 10 ml. of peppermint oil, accurately weighed, is added to 25 ml. of ½ N. alcoholic KOH. The mixture is refluxed on a water bath for exactly one hour and the excess KOH is titrated with ½N. sulfuric acid, using phenolphthalein as indicator. The esters present in the oil are calculated from the number of ml. of KOH consumed in the saponification as menthyl acetate.

b. Determination of total menthol. 10 ml. of peppermint oil, 10 ml. of acetic anhydride, and 1 gram of anhydrous sodium acetate are refluxed under boiling for exactly one hour. The mixture is washed with warm water and sodium carbonate solution until the last washing is alkaline to 2 drops of phenolphthalein. 5 ml. of the acetylated oil, dried with anhydrous sodium sulfate, is weighed and saponified with 50 ml. of ½N. alcoholic KOH for one hour and the excess KOH back titrated with ½N. sulfuric acid.

$$\% \text{ total menthol in oil} = \frac{A(7.813)}{B - A(0.021)} (1 - E \times 0.021)$$

where A = ml. of excess $\frac{1}{2}$ N. KOH

B = grams of acetylated oil taken

E = % esters calculated as menthyl acetate

2. Modified methods

The U. S. P. method for determination of menthol is slow and laborious so that a number of simplified methods has been recommended.

a. Using acetic anhydride and pyridine as reagents (18). A 0.6 gram sample of oil and 0.5 ml. of acetic anhydride are accurately weighed in a small test tube. After addition of 0.5 ml. of water-free pyridine, the tube is closed with a paraffin cork and set aside at room temperature for 48 hours. 50 ml. of water is then added and the mixture is titrated with $\frac{1}{2}$ N. KOH in a flask. Near the end point of the titration, the flask is heated 5 minutes over a water bath to ensure complete hydrolysis of the excess acetic anhydride and the titration is carried to the end point for phenolphthalein. The menthol content is calculated from the amount of acetic acid consumed.

b. Using acetic anhydride and n-butyl ether as reagents (6). To 1 gram of water-free oil add exactly 5 ml. of a mixture of 4 volume n-butyl ether and 1 volume acetic anhydride, reflux 1 hour, add 40 ml. water to decompose excess acetic anhydride and titrate the free acetic acid with $\frac{1}{2}$ N. alcoholic KOH using

phenolphthalein as indicator. Calculate the menthol from the amount of acetic acid combined.

3. Viscometric method

Peppermint oil is composed principally of menthol, menthone, menthyl esters, and hydrocarbons, all of which have approximately the same molecular weight and therefore might be expected to have the same effect on the viscosity of the oil. Because menthol is an alcohol, its OH group gives it a much higher viscosity than the other constituents. Since the viscosity of peppermint oil depends to a great extent upon the menthol present, this property can be used to estimate the composition.

Swift and Thornton (29) prepared a series of peppermint oils and plotted the time of draining of the oils from a 3-ml. Ostwald pipette against the menthol content. The percentages of free menthol content of unknown oils read from the chart were somewhat higher than the values obtained by chemical analysis and a correction factor should be applied for the interfering substances, which were correlated with the insolubility of the oil in a mixture of equal parts by volume of methyl alcohol and 70% ethyl alcohol. They reported that the results were in reasonably good agreement between the chemical and viscometric analysis.

4. Comparison of the different methods

In order to compare the relative accuracy of the above analytical methods, a series of artificial peppermint oils was prepared by mixing known weights of pure menthol with the first portion distillate from the natural oil containing 15.3% menthol analyzed by the U. S. P. method. The results by different methods are tabulated in Table V.

TABLE V

Comparison of Results by Different Analytical Methods

Menthol content	U.S.P. method	Error	Pyridine method	Error	n-butyl ether method	Error	Visco-metric method	Error
50.1%	51.3%	1.2	50.5%	0.4	49.5%	-0.6	52.4%	2.3
60.5	60.9	0.4	59.2	-1.3	59.8	-0.7	67.2	6.7
69.2	71.6	2.4	68.0	-1.2	67.0	-2.2	70.8	1.6
81.0	80.6	-0.4	79.2	-1.4	80.2	-0.8	---	---
100.0	96.4	-3.6	98.7	-1.3	95.0	-5.0	---	---

The pharmacopoeia method is regarded as the standard method of analysis but it did not always give the most accurate result. Baldinger (5) stated that the time of acetylation may vary without broad limits while the time of saponification had best be varied between 45 and 60 minutes to give results that did not deviate abnormally from the mean. If saponification is shorter than 45 minutes, the deviation from the mean

is usually negative; this indicates incomplete saponification; if it is longer than 60 minutes, the deviation is positive, which would seem to indicate the occurrence of side reactions involving KOH, possibly resinification of certain constituents.

Both pyridine and n-butyl ether methods gave slightly lower results but they were not less accurate than the U. S. P. method while much simpler in procedure. The above experiments proved that these two methods can be used satisfactorily in place of the official method. The pyridine method was used in most of the analysis in the present work because it is simple and convenient and because the results can be reproduced very closely.

The viscometric method can be used only as a rough approximation. It is not applicable to oils of high resin content because the resins greatly increase the viscosity of the oil. However, it is simple and rapid and can be used under conditions where the chemical method is impracticable.

B. Analysis of Menthone

Three methods of analyzing menthone were reported in the literature.

1. Hydroxylamine method

About 2 grams of peppermint oil is mixed with 15 ml. of a 5% solution of $NH_2OH \cdot HCl$ in 95% ethyl alcohol. The mixture

is heated gently to 100°C. on a water bath and the HCl liberated is titrated with ½ N. alcoholic KOH. The weight of menthone in the sample may be calculated from the ml. of alkali used. Methyl orange, dimethyl yellow, and bromophenol blue have been used as indicator in different laboratories (1)(3).

2. Semicarbazide method

Menthone reacts with semicarbazide hydrochloride quantitatively to form semicarbazone precipitate in the presence of sodium acetate. The menthone content is determined by weighing the dried precipitate (24).

3. 2,4-Dinitrophenylhydrazine method (14)

A crystalline precipitate in the form of 2,4-dinitrophenylhydrazone is obtained from water-alcohol solution of menthone. Menthone is precipitated quantitatively from dilute alcoholic solution by adding a 1.0-1.5% solution of 2,4-dinitrophenylhydrazine in 10% of sulfuric acid.

4. Choice of method

The hydroxylamine method was reported to give results which approximated very closely to the actual content. The writer found that bromophenol blue indicator was comparatively most satisfactory for oils of dark color but the end point was not very sharp. A sample of redistilled pure

menthone was used as a control test by adding calculated amount of alcoholic KOH to the neutral point and this solution was set aside as the standard of the end point. Baldinger (4) reported that the presence of various other constituents in the peppermint oil definitely affected the apparent menthone content from analysis and the percentage of menthyl acetate should be considered in determining the true menthone content. The hydroxylamine method using bromophenol blue as indicator was employed throughout this investigation.

C. Analysis of Resinous Materials (3)

5 ml. of oil, carefully weighed in a tared flask, are steamed distilled until all volatile materials have passed over. Remove the flask to an oven and maintain at a temperature between 90 and 100°C. After thorough drying, the flask is weighed. The difference in weight represents the amount of resinous material in 5 ml. of the oil.

This method was employed in determining the effect of temperature and time of heating on the resinification of the peppermint oil.

V. FRACTIONAL DISTILLATION

A. Boiling Points of Menthone and Menthol Under Reduced Pressures

The boiling points of pure menthol, menthone, and menthyl formate reported by Rochenberg (25) are shown in Table VII. To complete the data for menthol between the pressure range of 20 mm. and 700 mm. and to serve as a check, 20-gram samples of U. S. P. menthol melting at 42°C. and pure menthone were distilled in a 125 ml. distilling flask and the boiling points under various reduced pressures recorded. The results were in good agreement with the literature data and are shown in Table VI. The combined literature and experimental data are plotted in Figure I showing the relation between vapor pressure and temperature of these two compounds.

The boiling point difference of menthol and menthone is only 7°C. at atmospheric pressure while 15°C. at 20 mm. pressure. Menthone decomposes rapidly when boiling at atmospheric pressure as evidenced by the darkening of the liquid and the appearance of white fumes. Moreover, the rate of resinification of the peppermint oil was found to be slightly lower when refluxed at reduced pressure. Therefore, it was considered more advantageous to carry the fractional distillation at reduced pressure.

TABLE VI

Experimental Data of Boiling Points of Menthol and Menthone

Menthol		Menthone	
Pressure, mm. Hg.	B.P., °C.	Pressure, mm. Hg.	B.P., °C.
735	215	738	208
468	198	453	190
262	177	280	172
105	151	110	140
60	139	58	124
36	125	35	110
21	110	21	98

TABLE VII

Literature Data of Boiling Points of Menthol and Menthone (25)

Pressure, mm.	Boiling Point, °C.	
	l-Menthol	l-Menthone
760	216	209
800	218	---
700	212.70	206.20
600	---	200.00
500	---	192.60
400	---	183.80
300	---	173.00
200	---	159.05
100	---	137.48
90	---	134.40
80	---	130.90
70	---	127.30
60	---	123.20
50	---	118.45
40	---	112.50
30	---	105.10
20	111.00	96.05
15	105.30	89.61
10	89.20	81.60
8	94.25	77.25
6	89.45	71.80
5	86.50	68.40

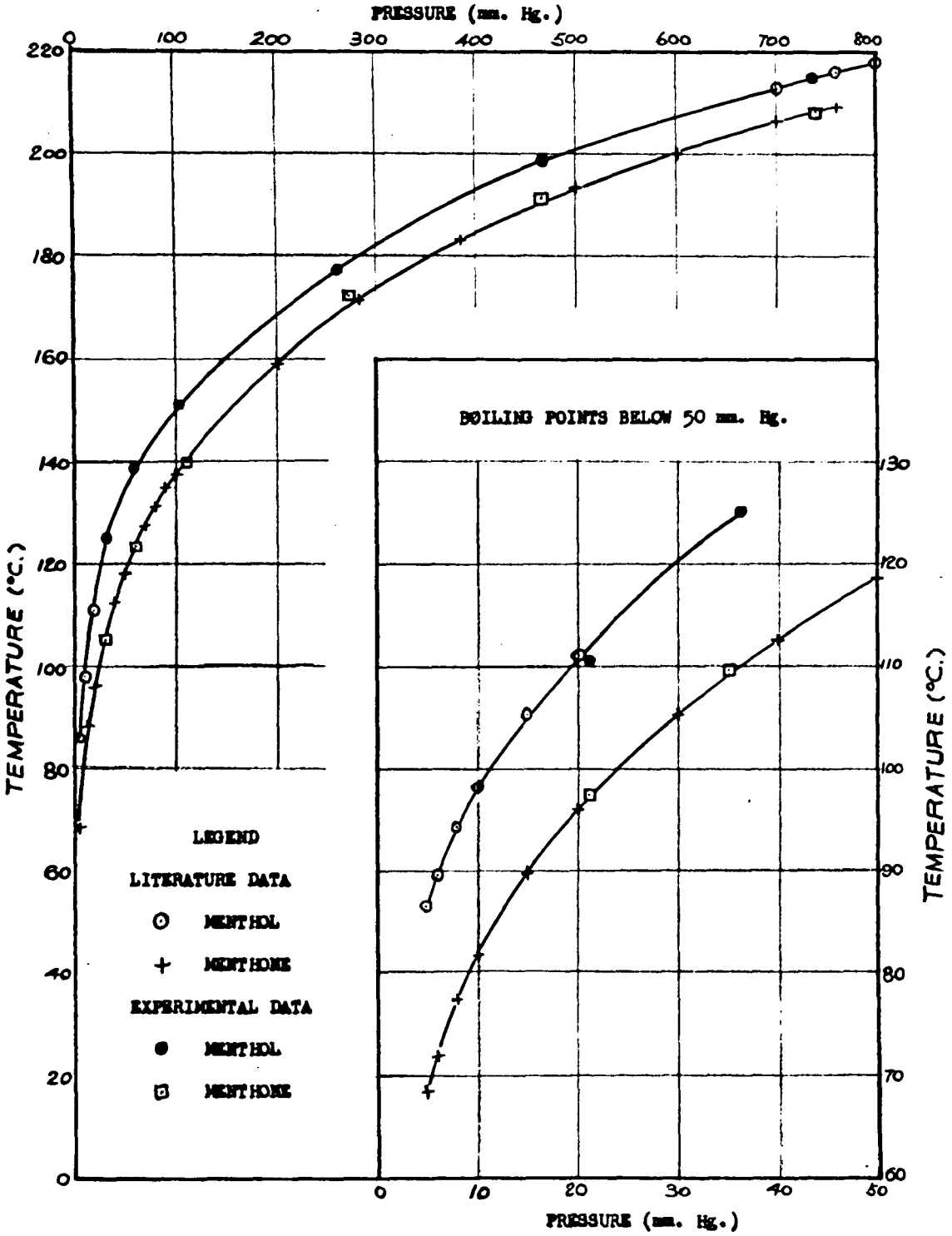


Figure I. Boiling Points of Menthol and Menthone at Reduced Pressures

B. Effect of Temperature and Time of Heating on Resinification of Peppermint Oil

1. Effect of temperature on resinification of peppermint oil

10-ml. samples of peppermint oil weighing 8.927 grams were refluxed to gentle boiling on an oil bath under different pressures for two hours. The resinous materials formed were determined by the steam distillation method. The results are listed in Table VIII and shown graphically in Figure II.

TABLE VIII

Effect of Temperature on Resinification of Peppermint Oil

Pressure	B.P.	Time	% Resinous materials
21 mm.	109-112°C.	2 hours	3.82
34	123-125	"	4.20
91	144-148	"	4.35
305	181.184	"	4.82
741	212-214	"	5.10

The curve is approximately a straight line indicating that the rate of resinification seems to increase linearly with increasing temperature. However, the effect is not very remarkable.

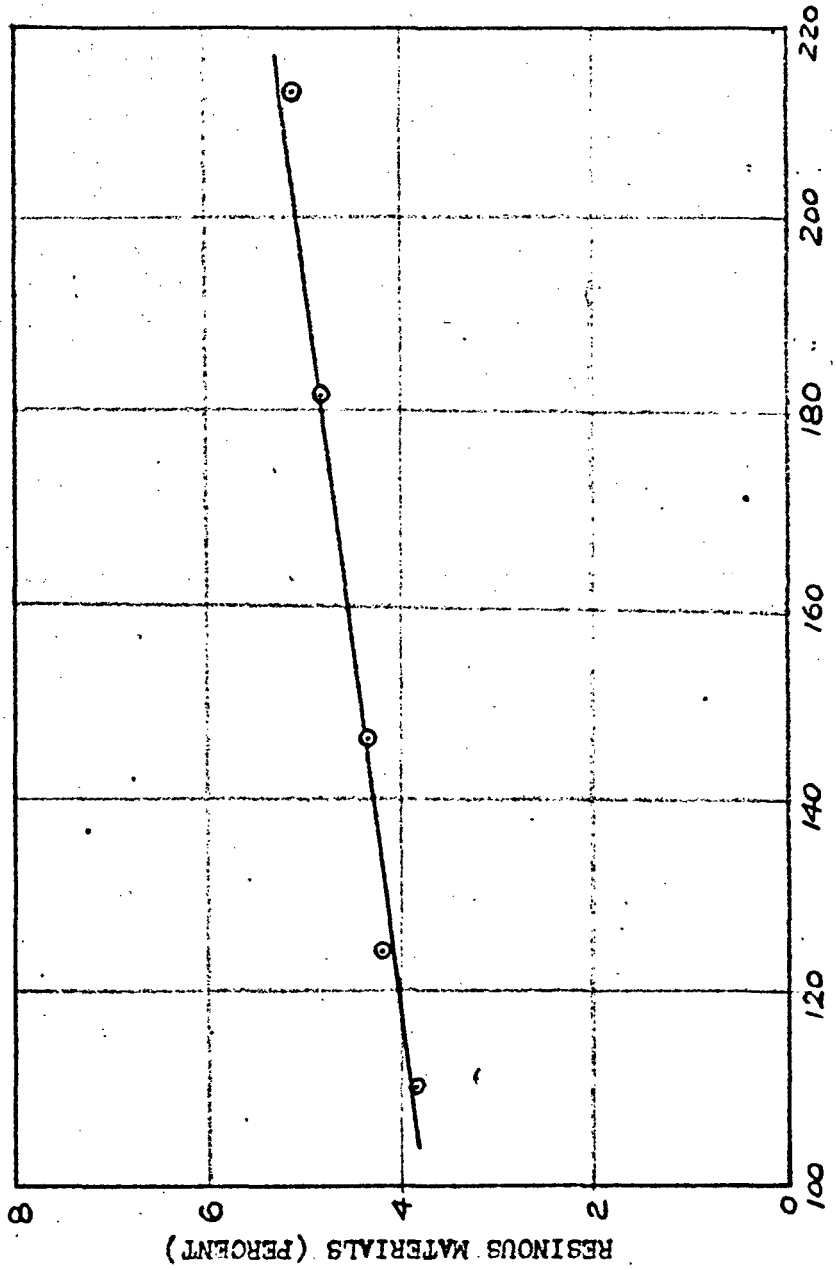


Figure II. Effect of Temperature on Resinification of Peppermint Oil

2. Effect of time of heating on resinification of peppermint oil

Similar experiments were performed using 10-ml samples of peppermint oil but refluxed to gentle boiling under atmospheric pressure for periods of ½ to 10 hours. The resinous materials formed were analyzed as before and the results are shown in Table IX and graphically in Figure III.

TABLE IX

Effect of Time of Heating on Resinification of Peppermint Oil

Time of heating	B. P.	% Resinous materials
½ hour	212-214 C.	1.08
1	"	2.32
1½	"	4.40
2	"	5.10
3	"	6.45
4	"	7.02
6	"	6.85
10	"	7.26

The curve begins to flatten after three hours heating. Further prolonged heating caused little increase of the resinous materials. Although menthol and menthone will form resinous materials to some extent, the resinification of the peppermint oil is mainly due to the various other constituents

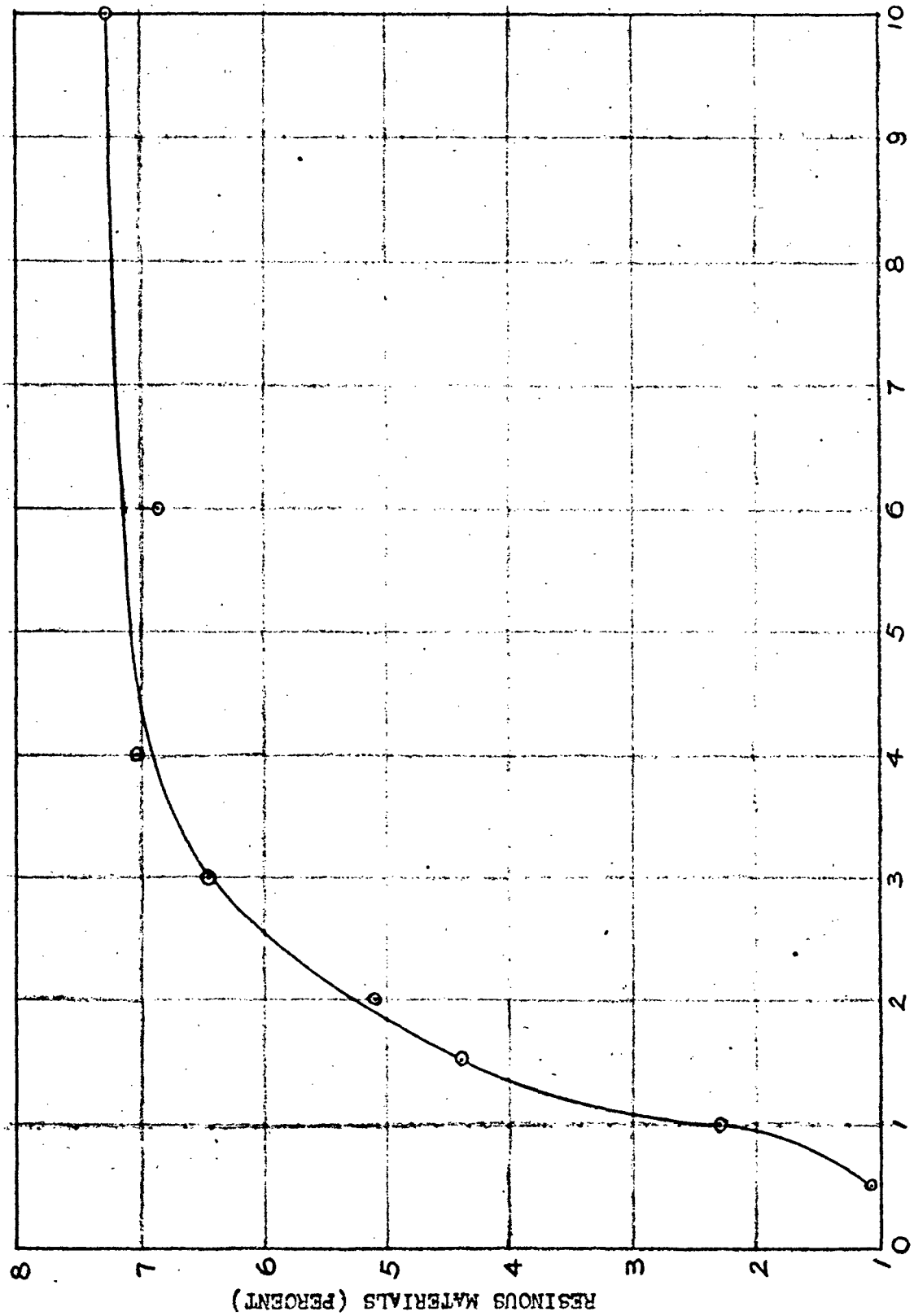


Figure III. Effect of Time of Heating on Resinification of Peppermint Oil

in the oil. The rate of resinification seems to slow down when most of these constituents have converted to resins.

C. Apparatus and Procedure for Fractional Distillation

The arrangement of apparatus is shown in Figure IV. The column, jacket, still pot, and condenser were all made of glass so that the operation of the column was completely visible. The fractionating column was constructed of 14 mm. inside diameter Pyrex glass tubing. It was packed with 3.2 mm. (1/8") inside diameter single-turn glass helices to a height of 131 cm. (51.6"). This column was first covered with aluminum paint leaving a narrow strip for observation purpose and then enclosed in an air jacket made of 25 mm. inside diameter glass tubing on which was wound about 40 feet of No. 24 Nichrome resistance wire to provide side heating. Outside of this jacket was a 40 mm. inside diameter glass tubing which served as further insulation.

The still pot was a 250 ml. or 500 ml. flask, depending on the amount of the charge, heated on an oil bath by a gas burner. A cooling finger at the top of the column served as a total condenser. All connections were made of 24/40 ground glass joints which were sufficiently air tight at a pressure of 20 mm. Hg.

The column was evacuated by a water aspirator which gave

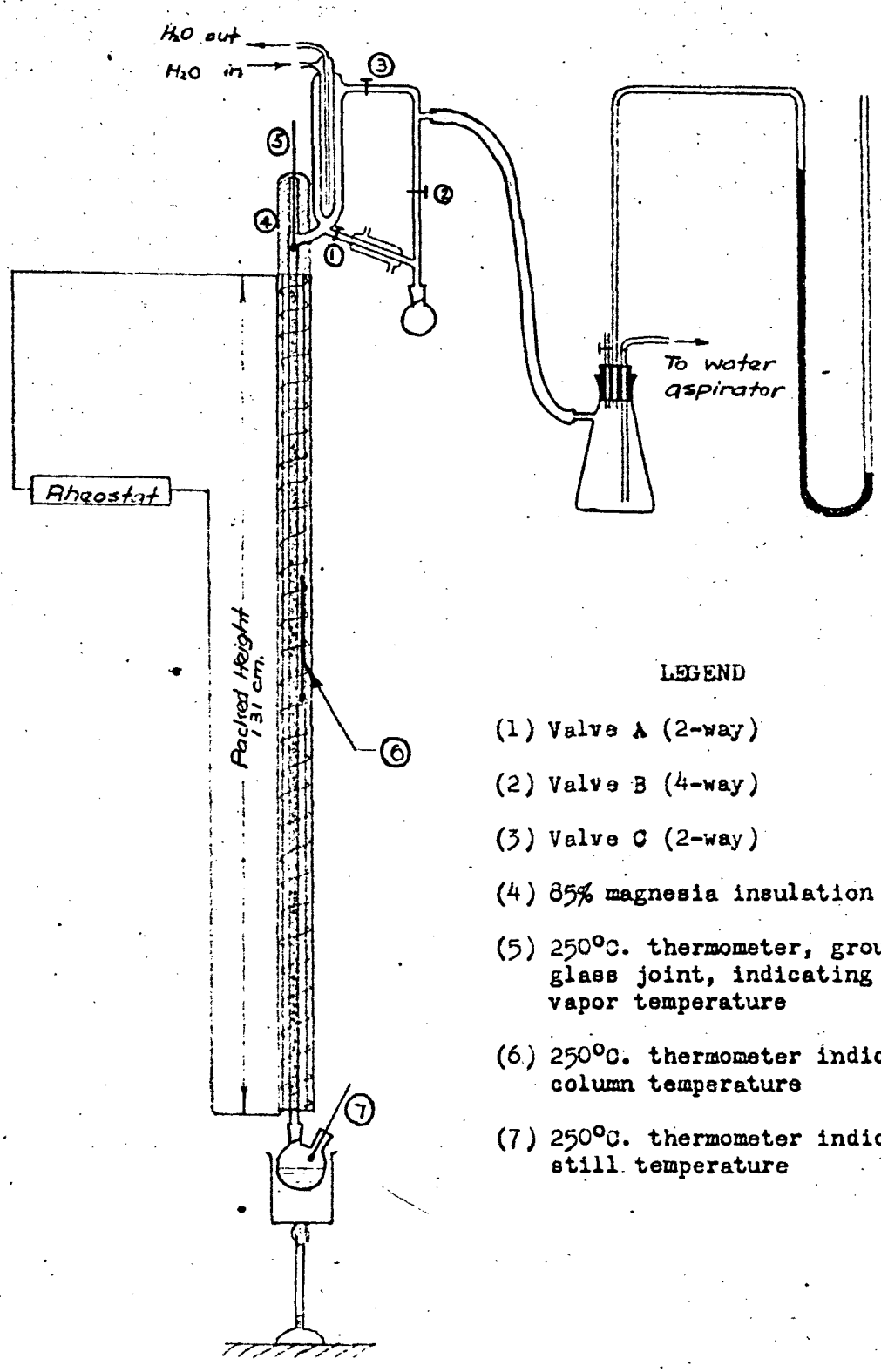


Figure IV. Appratus for Fractional Distillation under Reduced Pressure

an absolute pressure around 20 mm. Hg. The degree of vacuum obtainable depended on the temperature of the water but was maintained constant in any single distillation. Three thermometers were used indicating the vapor temperature, column temperature, and still pot temperature respectively.

Before starting the fractionation, the column was preheated approximately to the boiling point of the liquid to be distilled by careful control of a rheostat attached to the side heating. The still was then charged and a few small pieces of pumice were added to minimize bumping. Fenske and coworkers (11) reported that the efficiency of the column was greatly increased if the distillation was started with the packing thoroughly wet. Thorough wetting of the column was accomplished by deliberate flooding of the column at the start of the distillation and then the rate of boiling was decreased by adjusting the side heating and the burner. The still was then operated at a boiling rate just below flooding under total reflux for 2 hours to establish equilibrium. During this time the rate of boiling was kept as constant as possible. The reflux ratio was controlled by carefully adjusting the opening of the product stopcork A and was estimated by observing the number of drops of total condensate from the cooling finger and the number of drops of product withdrawn. This reflux ratio was only approximately correct. The volume of a single drop of liquid at a given temperature and pressure was not exactly the same but was affected by the size of the dropping

tip.

Distillate was collected corresponding as nearly as possible to the constant boiling fraction. When changing receiver, the product valve A was closed. The pressure within the receiver was restored to atmospheric by turning the four-way valve B while the vacuum in the column was undisturbed. Since menthol tended to solidify at room temperature, warm water at 50° to 60°C. was used in the condensers when menthol was distilled over.

D. Fractionation of Peppermint Oil

One hundred ml. of Chinese peppermint oil shipped from Shanghai, weighing 89.2 grams, was fractionated at a pressure of 21 mm. Hg. The sample was analyzed to contain 61.9% free menthol by the pyridine method and 15.8% menthone by the hydroxylamine method using bromophenol blue as indicator. The still temperature was gradually raised and the side heating was so adjusted that the column temperature was about 1 or 2 degrees Centigrade below the vapor temperature at the still. A reflux ratio of about 10 was used and small fractions with sharp boiling points were collected. The fractionation was carried out until no more distillate came over and the vapor temperature at the top of the column dropped rapidly while the still and column temperature rose to over 200°C.

The result of the fractionation is shown in Table X, and graphically in Figure V in which the accumulative volume

percent of distillate is plotted against the vapor temperature at the top of the column. The menthol contents of the fractions were analyzed by the pyridine method.

The menthol fractions solidified into an amorphous mass on cooling and deposited long needle-form crystals on the wall of the container. It melted at 38 to 42°C. which did not conform with the U. S. P. specification of 41 to 43°C.

The fractions 12 and 13 (B. P. 106 to 110°C.) were combined and refractionated under 21 mm. pressure. The fraction boiling at 110°C. was collected. It solidified to a crystalline powder. The melting point was 41 to 42°C. which met the U. S. P. requirement. The yield was about 43 grams, or 48.2% of the weight of the peppermint oil taken. In other words, 78% of the menthol contained in the oil was recovered as U. S. P. menthol.

This crystalline powder was recrystallized from 95% ethyl alcohol. The crystals obtained still melted at 41 to 42°C., which seem to indicate no further improvement in quality, although the powder was transformed to long needle-like crystals. l-Menthol did not racemize during fractionation because the melting point of the racemic mixture of d- and l-menthol would be only 27-28°C.

TABLE X

Fractionation of Peppermint Oil

Fractions	B.P.	Distillate ml.	Cumulative Vol. %	% Menthol
1	55.5-56.5°C.	0.8	0.8	
2	64	0.5	1.3	
3	71-71.5	1.7	3.0	
4	74.5-75	1.5	4.5	
5	78.5-79	1.0	5.5	
6	86.2-87	0.6	6.1	
7	89-90	4.0	10.1	
8	92-93	1.4	11.5	8.15
9	95.5-96	5.9	17.4	7.24
10	96	5.1	22.5	7.65
11	98-100	0.6	23.1	66.5
12	106-108	2.3	25.4	83.6
13	110	58.8	84.2	95.8
14	115-116	2.3	86.5	9.2
15	120-121	1.1	87.6	
16	133	0.8	88.4	
17	144	0.4	89.8	
18	149-150	0.4	90.2	
19	Residue	7.9	98.1	
Total			98.1	

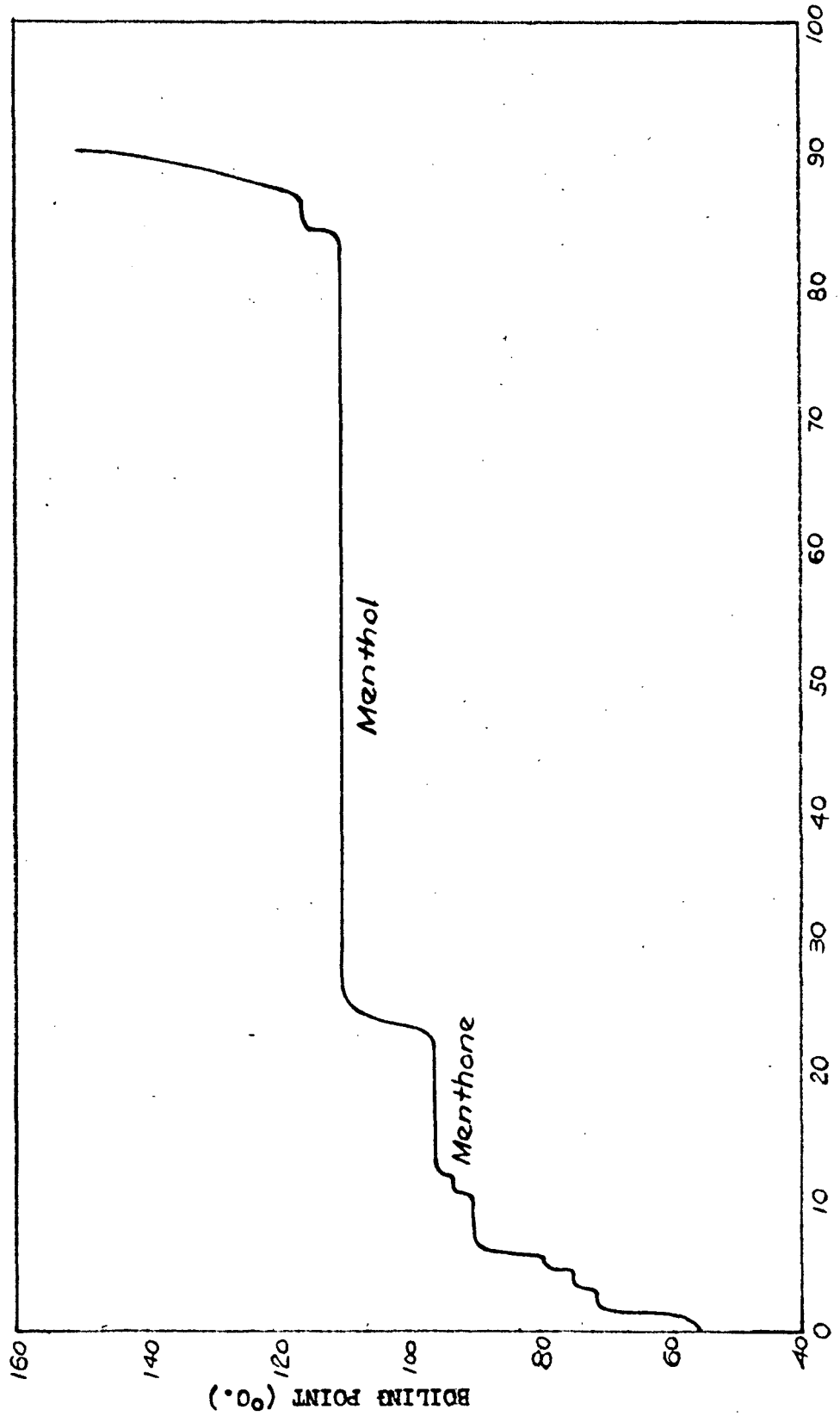


Figure V. Fractionation of Peppermint Oil.

E. Fractional Distillation of Menthone from Peppermint Oil

Another 100 ml. sample of the same oil was fractionated at the same pressure of 21 mm. Hg. under the same conditions as the previous fractionation but this time the distillation was carried only to 96°C. where most of the menthone was distilled over. The distillation was stopped as soon as the vapor temperature at the top of the column rose suddenly to 100°C. After the pressure in the column had been brought to atmospheric, the column temperature was maintained at 50°C. for two more hours by adjusting the side heating to prevent the menthol from solidifying in the column during the draining. After standing overnight, the column was cleaned by passing compressed air to reduce the holdup as much as possible.

The first two portions of menthone distilled over were analyzed to contain over 100% menthone which would seem to indicate that these fractions were pure menthone. The analytical results of various fractions are shown in Table XI.

The residue solidified at room temperature. About 20 grams of this residue was recrystallized from alcohol and 5.6 grams of long needle-like crystals was obtained. The crystals melted at 41 to 42°C. which was within the melting point range specified in United States Pharmacopoeia.

TABLE XI

Fractional Distillation of Menthone from Peppermint Oil

Fractions	B.P.	ml.	% Menthol	% Menthone
1	Below 94°C.	11.8	---	---
2	94.5-95	2.0	---	100.5
3	95-96	9.2	---	101.8
4	96	4.0	3.0	98.8
5	Residue above 100	71.5	90.2	1.4
	Total	98.5		

The yield of menthol by recrystallization cannot be calculated from the above data because the alcohol was saturated with menthol. This mother liquid may be used over and over again until the resin content becomes so high as to interfere with the crystallization.

The resin in the residue may be removed by steam distillation. A ten-gram sample of the residue was weighed in a tared flask and steam distilled until all volatile materials had passed over. The flask was placed in a water bath which served as a good insulation and supplied part of the latent heat required for the volatile materials. By this means, the amount of direct steam consumed was reduced so that the loss of

menthol in the aqueous layer was minimized. The flask was then dried in an oven for 24 hours at 100°C. and weighed. The resinous materials was found to be 4.05%. The menthol was separated from the aqueous layer and recrystallized from alcohol. The melting point was 42 to 43°C.

F. Test of the Column

1. Test mixture

Carbon tetrachloride and benzene were used as the binary mixture in testing the number of theoretical plates in this laboratory fractionating column. This mixture was used because it is cheap and readily obtained in the pure state. The boiling points of carbon tetrachloride and benzene are 76.75 and 80.1°C. respectively under 760 mm. Hg. so that this mixture may be used for columns having a large number of plates. All physical constants and vapor-liquid equilibria data are available in the literature. The two liquids form a constant boiling mixture at 91.65 mole % carbon tetrachloride (12) but this difficulty was avoided by proper choosing of the concentrations of the two liquids so as to operate in the middle portion of the x-y diagram.

2. Test procedure

The column was carefully cleaned by refluxing acetone

for two hours. After complete draining, the column was heated to 80°C. for two hours to remove all acetone. About 100 ml. of carbon tetrachloride and 200 ml. of benzene were then charged into a 500-ml. flask, which served as a batch distilling still. The fractionation was carried out at atmospheric pressure (742 mm.) for two hours under total reflux to establish equilibrium, during which time the boiling rate was held constant at just below flooding. Vapor temperatures of still pot and column head were recorded as 78.0 and 75.8°C. respectively. After equilibrium had been established and with the column operating, 3-ml. samples of the still liquid and distillate were withdrawn within as short an interval of time as possible. The samples were first cooled to 20°C., drawn into 2-ml. pipettes, and then accurately weighed.

3. Analysis

The analysis of the mixture was made by measuring the density at 20°C. The composition was calculated from the equation given by Fenske and coworkers (11):

$$d = 0.8795 + 0.7740x - 0.05654\ x^2$$

where d = density of carbon tetrachloride-benzene mixture at 20°C.

x = weight fraction of carbon tetrachloride in the mixture.

Density of pure carbon tetrachloride = 1.597 g./ml. at 20°C.

Density of pure benzene = 0.8795 g./ml. at 20°C. The equation was claimed to be accurate within 5 parts per ten thousand. The analytical results were as follows:

TABLE XII

Analytical Results of CCl_4 and C_6H_6 Test Mixture

	Distillate	Residue
Density at 20°C.	1.3886	1.1069
Mole fraction of CCl_4	0.694	0.301
Mole fraction of C_6H_6	0.306	0.699

4. Calculations

The number of theoretical plates of this column was calculated by two methods:

a. Using Fenske formula. Fenske and coworkers (13) developed an algebraic method of calculating the minimum number of theoretical plates by utilizing the relative volatility together with the fact that at total reflux the operating line becomes the x-y diagonal in the McCabe-Thiele diagram.

$$\frac{(X_a)}{(X_b)_D} = \alpha^{n+1} \frac{(X_a)}{(X_b)_R}$$

where X_a = mole fraction of component a

X_b = mole fraction of component b

sub D = in distillate

sub R = in residue

$\alpha = \frac{P_a}{P_b}$ = relative volatility at the mean distillation temperature

P_a = vapor pressure of pure compound a at that temperature

P_b = vapor pressure of pure compound b at that temperature

This formula offers a simple and rapid means of determining the number of theoretical plates at total reflux and avoids the necessity of constructing the x-y diagram. In general, an arithmetical average of the relative volatility at the temperature of the still and the temperature at the top of the column is satisfactory. This formula is based on the usual assumptions that the liquids obey the Raoult's law and the molal overflow is constant. This method is particularly useful when the number of theoretical plates is very large where the graphical stepwise method cannot give a reliable answer.

The average relative volatility was calculated based on the vapor pressure data of carbon tetrachloride and benzene given in Lange Handbook (19);

Vapor pressure of C_6H_6 at $70^{\circ}C.$ = 547.4 mm.
" " " " " $80^{\circ}C.$ = 753.6 mm.
By interpolation, " " " " " $75.8^{\circ}C.$ = 667 mm.
" " " " " $78.0^{\circ}C.$ = 712 mm.

Vapor pressure of CCl_4 at 70°C. = 622.3 mm.

" " " " " 76.75°C. = 760 mm.

" " " " " 80°C. = 843 mm.

By interpolation, " " " " " 75.8°C. = 741 mm.

" " " " " 78.0°C. = 792 mm.

α at 75.8 C. = 741/667 = 1.09

α at 78.0 C. = 792/712 = 1.11

α average = 1.10

Substituting the α average and the analytical results into Fenske's formula, the answer is:

$$\left(\frac{0.694}{0.306}\right) = (1.10)^{n+1} \quad \frac{(0.301)}{(0.699)}$$

n = 16.4 theoretical plates

b. Using McCable-Thiele graphical method. The vapor-liquid equilibria data of carbon tetrachloride and benzene mixture at atmospheric pressure were worked out by Rosanoff and Easlay (26):

TABLE XIII

Vapor-Liquid Equilibria Data of CCl_4 and C_6H_6

B.P. °C.	Mole fraction of CCl_4 in liquid (x)	Mole fraction of CCl_4 in vapor (y)
80.23	0	0
79.36	0.1364	0.158
78.82	0.2157	0.242
78.62	0.2573	0.288
78.48	0.2944	0.321
78.15	0.3634	0.392
77.97	0.4057	0.435
77.57	0.5269	0.549
77.23	0.6202	0.639
77.07	0.7223	0.733
76.69	1.0000	1.000

Using these data and the McCabe-Thiele graphical method, the number of theoretical plates was figured out to be 16.8.

c. Discussion. The small difference in the number of theoretical plates found by two methods was due to the data of vapor pressure and vapor-liquid equilibria taken from different sources.

The average number of theoretical plates was 16.6 while the height of the packed column was 51.6 inches. The H. E. T. P. (height equivalent to a theoretical plate) was 3.11 inches for this column.

The H. E. T. P. was known to vary quite appreciably with the test liquids used and carbon tetrachloride-benzene mixture usually gave low values of number of theoretical plates or high values of H. E. T. P. Tongberg and coworkers (31) reported that for a laboratory column having 10 mm. inside diameter and 16 inches packed height packed with 1/8" single-turn glass helices, the H. E. T. P. was 2.0 to 2.3 inches using CCl_4-C_6H_6 test mixture but only 1.4 to 1.55 inches using n-heptane and toluene as test mixture.

The efficiency of the packed column decreases rapidly on increasing the column diameter and packed height. With the same kind of packing, Fenske and coworkers found that the H. E. T. P. was 5.7 to 6.7 inches for a column having 32 mm. inside diameter and 2.74-meter packed height.

VI. DISCUSSION

In view of the preceding experimental results, it is seen that menthol can be separated from peppermint oil by fractional distillation either by first removal of menthone followed by crystallization or by directly distilling over menthol.

The fractionation can be completed in a much shorter time if it is carried out only up to the point where menthone and other low boiling fractions are distilled over. The capacity of a given column will be greatly increased and cost of heating will be considerably reduced. Since most other constituents in peppermint oil are more volatile than menthol, the residue left after removal of menthone will contain about 90% menthol. This menthol may be obtained in pure crystalline form by crystallizing from a suitable solvent, such as ethyl alcohol. The mother liquid will retain a large amount of menthol but it can be used as fresh solvent repeatedly until the resin content in the liquid becomes so high as to require purification. The alcohol then can be easily distilled off and the menthol can be separated from the resins by steam distillation. In this manner, most of the menthol in the residue may be recovered. This process will produce menthol in the form of long needle-like crystals which is preferred in the trade although this demand may not be logical.

In the case that fractionation is carried out until all

the menthol has been distilled over, a much longer time is needed. After a second fractionation of the menthol fraction, the product obtained was within the melting point range of U. S. P. quality menthol. Due to the construction of the distilling head, a reflux ratio larger than 10 could not be maintained for this column. If a larger reflux ratio were used, a single fractionation would be able to effect the desired separation. Seventy-eight percent of the menthol contained in the peppermint oil was recovered in this experiment and an improvement of the yield may be expected if the fractions boiling close to the menthol were charged to the second batch and refractionated again, or a larger reflux ratio were employed. This process seems to be simpler and may be expected to give a higher yield than the crystallization process.

Menthone is the main by-product of the fractionation. While the price quoted for menthone is considerably higher than that of menthol, there is very little demand for menthone at the present time except in chemical laboratories. However, this menthone is free from the unsaturated constituents present in the oil and can be converted into menthol by reduction which is much easier to be controlled than the reduction of peppermint oil as previously discussed. The yield of menthol from peppermint oil can be further increased if the reduction can be carried out successfully.

The first cost of a plant producing menthol will be small compared with the working capital required. For example, if a plant producing 300 pounds of menthol daily or about 100,000 pounds per year, the annual sales will be about $900,000 while the first cost of such a small plant will be only a few percent of the annual sales. Some idea of the cost of raw material and the value of the product may be had from the following estimates, which are based on the assumption that 80% of menthol in the oil can be recovered.

(1) Assume peppermint oil containing 60% menthol is used as raw material.

Basis: 1 pound of peppermint oil

Value of product: 0.48 lb. menthol at $9.00	$4.32
Cost of oil: 1 lb. peppermint oil at $2.50	$2.50
Margin:	$1.82 per lb. of oil.
	or $3.80 per lb. of menthol made.

(2) Assume dementholized oil containing 50% menthol is used as raw material.

Basis: 1 pound of dementholized oil

Value of product: 0.40 lb. menthol at $9.00	$3.60
Cost of oil: 1 lb. dementholized oil at $2.25	$2.25
Margin:	$1.35 per lb. of oil.
	or $3.38 per lb. of menthol made.

The cost of the peppermint oil is based on the actual cost of a sample recently received from Shanghai, China. The cost of the dementholized oil is estimated to be one-fourth of the cost of menthol (21). The above margin should be ample to cover the processing cost.

For commercial operation, a bubble-cap column may be more efficient than a packed column since the efficiency of packed columns is greatly decreased for columns having large diameters. The boiling point difference of menthol and menthone is 15°C. at 20 mm. while 12°C. at 50 mm. Hg. An absolute pressure of about 2 inches Hg. is readily obtainable and may be more suitable for larger scale fractionation.

Future research should be carried out on the fractionation of menthol in a larger column using larger reflux ratios to obtain data required for design purposes and on the reduction of menthone to menthol either by reducing agent, such as aluminum isopropylate, or by catalytic hydrogenation.

VII. CONCLUSIONS

1. The analysis of menthol in peppermint oil using pyridine and acetic anhydride as acetylation reagents is more convenient than other methods and the results were not less accurate than the U. S. Pharmacopoeia official method.

2. The analysis of menthone in peppermint oil by the hydroxylamine method using bromophenol blue as indicator is recommended.

3. The boiling point difference of menthol and menthone is much greater at reduced pressures than at atmospheric pressure.

4. These two compounds may be separated from peppermint oil by fractionation in an efficient column under reduced pressures.

5. Seventy-eight percent of the menthol contained in peppermint oil was recovered in pure crystalline state by fractionation alone.

6. The purity of menthol produced either by fractionation alone or followed by crystallization from alcohol meets the melting point specification of U. S. P.

7. l-Menthol will not change to a racemic mixture by heating during the fractional distillation.

8. The rate of resinification of peppermint oil increases slightly with increasing temperature.

9. The resinous materials formed will not further increase after four hours of heating under atmospheric pressure.

10. A new process of producing menthol from peppermint oil by fractional distillation seems to be economically feasible.

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